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For the purpose of structural determination of molecular adsorbates with large unit cells or lattice-gas disorder on metal surfaces, a novel method was developed to handle multiple scattering of electrons by surfaces. The method is particularly suitable for complex and disordered surfaces. It enables a great increase in computational efficiency for the determination of surface structures. In particular, a method of treating electron scattering by chains of atoms (these chains are to be thought of as components of a surface) was developed. These new methods were applied to the interpretation of experimental data, thereby extracting structural information about simple but non-trivial surfaces.		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
The key to the approach is twofold: first, use kinetic electron energies above a few hundred electron volts, so as to obtain forward focusing by atoms; second, treat the surface as a cluster of atoms without regard to periodicity, thereby allowing complex and disordered surface structures.		22a. NAME OF RESPONSIBLE INDIVIDUAL	
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"Local Structure of Disordered Monolayers of Molecules on Metal Surfaces", M.A. Van Hove, M.L. Xu, G.S. Blackman, D.F. Ogletree and G.A. Somorjai, to be published in Proceedings of the Scientific Conference on Chemical Defense Research, CRDEC-SP-xxxxx (1988).

"Disordered Asymmetrical Adsorption Structures of Clean Mo(100)-(1x1) and of 'c(2x2)' Sulfur on Mo(100) from Dynamical LEED Analyses", D.G. Kelly, R.F. Lin, M.A. Van Hove and G.A. Somorjai, submitted to Surface Science.

"Automated Structure Search with Tensor LEED Applied to Carbon and Sulfur Adsorption on Mo(100)", P.J. Rous, D.G. Kelly, M.A. Van Hove and G.A. Somorjai, in preparation.

8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED:

Dr. J.J. Barton,

Dr. R.F. Lin,

Dr. P.J. Rous,

Dr. M.L. Xu,

Dr. M.A. Van Hove



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BRIEF OUTLINE OF RESEARCH FINDINGS

For the purpose of structural determination of molecular adsorbates with large unit cells or lattice-gas disorder on metal surfaces, we have developed a novel method to handle multiple scattering of electrons by surfaces. The method is particularly suitable for complex and disordered surfaces. It enables a great increase in computational efficiency for the determination of surface structures. In particular, we have developed a method of treating electron scattering by chains of atoms (these chains are to be thought of as components of a surface).

We have successfully applied these new methods to the interpretation of experimental data, thereby extracting structural information about simple but non-trivial surfaces.

The key to our approach is twofold: first, we use kinetic electron energies above a few hundred electron volts, so as to obtain forward focusing by atoms; second, we treat the surface as a cluster of atoms without regard to periodicity, thereby allowing complex and disordered surface structures.

A theory called "Near-Field Expansion in Clusters" was developed. It selects only important scattering events in such a way that the computing effort is proportional to the electron wave number. Conventional LEED-style methods scale as at least the fourth power of the wave number. This removes the most serious barrier to the analysis of electron diffraction at higher energies. In the case of Low- and Medium-Energy Electron Diffraction, this approach enables a better understanding of the multiple-scattering events that occur at surfaces.

The method was next extended to emphasize chain effects, namely to investigate how chains of atoms focus electrons in the chain direction. It has been applied to several techniques involving diffracted electrons. With Medium-Energy Electron Diffraction we found definite chain-focusing effects. These were modulated by strong interference effects. Both types of effect could be used to determine surface structures. In fact, the best application is for disordered surfaces, our main goal. However, we found a helpful simplification if we took

electrons generated in a different way, such that incoherent emission from each surface atom can be assumed. This situation applies to the techniques of angle-resolved x-ray photoelectron emission, of angle-resolved Auger electron emission and of angle-resolved inelastic electron scattering ("Kikuchi-like" electron emission). Disorder is easily treated with these techniques as well.

Previous experimental work with these techniques exists in the relevant energy range. Simple calculations by others have predicted some of the main observed features, but point to the necessity of including multiple scattering effects. Our theory is perfectly designed to do this and we have been able to reproduce experiment for the first time within the experimental uncertainty. More important is the finding that observed peaks of electron emission indeed are directed along chains of surface atoms, but that some of those peaks are interference effects that only indirectly indicate the direction of atomic chains. We have thereby established that our approach gives an excellent structure-sensitive tool. Two advantages over other methods stand out: relatively fast computations and no need for synchrotron radiation.

The technique which we have applied has gained much popularity as an effective method of surface structure determination. This illustrates its potential which could be developed further for different applications.

In the next phase of the work, we have dealt more specifically with structure determination from "diffuse LEED" for disordered surfaces. The theory has been programmed by us and experimental data obtained by the group of Professor Somorjai in Berkeley.

The theory is based on the successful "beam-set neglect" method of LEED calculations. It was introduced in the past by us to tackle complex surface structures, in particular for molecular overlayers. It now finds a new application in the case of disordered overlayers. The soundness of the method has been checked against a more exact but much more computer-intensive method. Computing efficiency is of the utmost importance in structure determination, since one normally has to check out many different candidate structures, and each one requires a full computation.

The experiment (not part of this ARO grant, but crucial to its success) involves a novel type of position-sensitive LEED detector. It combines a "wedge and strip" detector with multichannel plates, and involves real-time microcomputer data processing. This study is its first application. The new detector is ideally suited to the task of measuring the relatively weak diffuse intensity due to disordered surface structures. In addition, the new detector allows ultra-weak electron beams to be used, which eliminates the customary high risk of beam-induced damage to molecular layers.

The surface chosen for our study is carbon monoxide on Pt(111), which provides an excellent and realistic prototype for disordered molecular overlayers. We were extremely pleased that we could, for the first time in surface crystallography of disordered molecular adsorbates, determine their detailed bonding arrangements: bond lengths, bond angles, adsorption sites, and even the distribution among different, simultaneously occupied adsorption sites. We could compare the new results with previous results for the ordered case, and we found very good agreement, thereby reinforcing our confidence in this new approach.

We have also analyzed the structure of disordered benzene adsorbed on the Pt(111) surface. The structure that we obtained is very satisfactory, as it fits our expectations in various ways. We have found that to obtain details of the distortions within the benzene, however, our experimental data base was not quite sufficiently large. The experimentalists are therefore at present extending their measurements and a final analysis is about to take place.

It is already clear from our most recent work that the technique will be able to deliver the desired information. That was exactly the purpose of this project. We know this also from recent analyses of atomic adsorbates (obtained by molecular decomposition). Specifically, we have studied the structure of sulfur atoms adsorbed on Mo(100) (a very useful model for the important MoS₂ catalyst). They present disorder and induce relaxations in the metal lattice itself. We have been able to analyze these details in large part through the development of an automated structural search technique (previously, one had to laboriously fit each unknown structural parameter to the experimental data).